# How Close to Two Dimensions Does a Lennard-Jones System Need to Be to Produce a Hexatic Phase?

Nadezhda Gribova,[1, 2, 3, a)] Axel Arnold,[4, 5] Tanja Schilling,[6] and Christian Holm[4]

[1)] *Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, D-70569 Stuttgart, Germany*

[2)] *present address: Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, Pfaffenwaldring 9, D-70569 Stuttgart, Germany*

[3)] *Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 142190, Moscow Region, Russia*

[4)] *Institute for Computational Physics, University of Stuttgart, Pfaffenwaldring 27, D-70569 Stuttgart, Germany*

[5)] *previous address: Fraunhofer SCAI, Schloss Birlinghoven, D-53754 Sankt Augustin, Germany*

[6)] *Université du Luxembourg, 162 A, avenue de la Faïencerie, L-1511 Luxembourg*

(Dated: 18 January 2013)

We report on a computer simulation study of a Lennard-Jones liquid confined in a narrow slit pore with tunable attractive walls. In order to investigate how freezing in this system occurs, we perform an analysis using different order parameters. Although some of the parameters indicate that the system goes through a hexatic phase, other parameters do not. This shows that to be certain whether a system has a hexatic phase, one needs to study not only a large system, but also several order parameters to check all necessary properties. We find that the Binder cumulant is the most reliable one to prove the existence of a hexatic phase. We observe an intermediate hexatic phase only in a monolayer of particles confined such that the fluctuations in the positions perpendicular to the walls are less then 0.15 particle diameters, i. e. if the system is practically perfectly 2d.

[a)]Electronic mail: gribova@icp.uni-stuttgart.de

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## I.  INTRODUCTION

Understanding the structure and dynamics of confined fluids is important for processes such as wetting, coating, and nucleation. The properties of a fluid confined in a pore differ significantly from the bulk fluid due to finite size effects, surface forces and reduced dimensionality. In this work we report on a study of one of the simplest models that is still capable of reproducing the thermodynamic behavior of classical fluids, the Lennard-Jones (LJ) system. The LJ potential is an important model for exploring the behavior of simple fluids and has been used to study homogeneous vapor-liquid, liquid-liquid and liquid-solid equilibrium, melting and freezing[1–3]. It has also been used as a reference fluid for complex systems like colloidal and polymeric systems.

The vapor-to-liquid transition in confined systems has been studied intensively, and is well understood (see[4] and references therein). In this article we will discuss the liquid-to-solid transition in a slit pore and the process of the development of the solid phase. In the liquid phase, confinement to a slit induces layering at the walls. One could imagine this effect to facilitate crystallization. And indeed it is known that depending on the strength of the particle-wall interaction, the freezing scenario changes significantly[1,5]. If the walls are strongly attractive, crystallization starts from the walls and at a temperature higher than without confinement. If the walls are strongly repulsive, crystallization starts from the bulk at a temperature lower than without confinement.

A well-distinguished layer of particles close to the wall can also, to some extent, be treated as a 2d system. The melting of true 2d systems has been studied both theoretically[6–10] and experimentally[11–13]. A large number of experiments on 2d melting were carried out in colloidal systems where colloidal particles contain a magnetic core, giving rise to a magnetic repulsion between particles that can be controlled by an external magnetic field (see, for example,[14–16]). The type of the scenario strongly depends on the shape of the potential. Soft-core potentials melt via the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) mechanism[7,9], meaning that the liquid turns into a crystal going through an intermediate hexatic phase[17–21]. For the hard disks system two different points of view exist[7,8,10,22]. Since the Lennard-Jones potential is rather soft, the freezing of a single layer of LJ particles can therefore be expected to proceed via the KTHNY mechanism[23], which significantly differs from the bulk nucleation scenario.

As we will show, it can be difficult to check whether the hexatic phase exists. To solve this problem several order parameters to characterize the bond-order were introduced in the literature. The correlation function of the local bond-order parameter[21] that measures the nearest-neighbor-bond-angular order is commonly used. However, it can not distinguish between a hexatic phase and a heterogeneous system in the two-phase region. The distribution of the bond-angular susceptibility on various length scales was introduced to overcome this problem studying a hard disks system and Lennard Jones disks[24]. Later the search for a general and efficient method to determine all phases and bounds of the transition was continued. The scale analysis of the behavior of the fluctuation of the bond-angular susceptibility and the bond-orientation cumulant provided[25] an evidence of a possible continuous transition in the system of hard disks[10]. To our knowledge, the Binder cumulant was applied in the analysis of the existence of the hexatic phase only for 2d systems and never for quasi-2d or 3d. The analysis of fluctuations of the bond-angular susceptibility within a layer was used already for studying the melting of thin films up to 20 layers[26]. A modified scaling analysis of the bond-angular susceptibility[27] was used not to check the existence of the hexatic phase only in 2d systems[8,27,28], but also in quasi-2d systems, for example[29].

This raises the question, how the crystallization in a strongly confined quasi 2d system proceeds, i. e. a system only a couple of particle diameters wide. In this case, it is not clear whether the system still behaves like being truly two dimensional, or whether it rather behaves similar to a bulk system. The solid-solid phase transitions of confined fluids in narrow slit pores were studied both at zero and at finite temperatures (see References[30–32] and references therein). For a confined LJ fluid, the question if a hexatic phase exists in a quasi 2d system has been studied by Radhakristan and coworkers[33] for a ratio of wall-particle to particle-particle attraction varying between 0 and 2.14 and pores widths of 3 and 7.5 fluid particle diameters. For the narrower slit pore it was shown that around the freezing temperature the system exhibits a hexatic phase. With increasing wall attraction this temperature region becomes wider, i. e. an attractive wall facilitates the formation of the hexatic phase. The phase diagram for the wider pore with diameter 7.5 is more complicated. When the wall-particle attraction becomes bigger than the particle-particle attraction, at first a hexatic phase and then a crystal phase appear, however, only in the contact layers near the walls; the rest of the system remains liquid. Only when decreasing the temperature further the system crystallizes completely. The temperature range, in which hexatic or

crystal phases are observed only in the contact layers, again widens with growing wall-particle attraction. This indicates that the wall-particle attraction facilitates the formation of a hexatic phase even in wider pores, however only in the layers close to the walls. The same group of authors also reported that in a pore, that can accommodate only a single layer, two second order transitions are observed, while already in a pore wide enough to accommodate two layers, both transitions are of the first order [29].

The different crystal structures of the frozen phase were studied by Vishnyakov and Neimark[34] as a function of the size of the slit for this system. The distance between the walls was gradually increased up to a slit accommodating three layers. Depending on the width of the pore, hexagonal or orthorhombic phases were observed in the layers.

In a recent article by Page and Sear[35] it was shown that freezing is controlled by pre-freezing in a similar system. Nucleation of the bulk crystal is affected by the surface phase behavior. With increasing wall attraction, the bulk nucleation is smoothly transformed into nucleation of a surface crystal layer. Xu and Rice[36] investigated theoretically a quasi 2d system of hard spheres and reported the dependence of the density at the liquid-to-hexatic phase transition on the thickness of the system, with wall separation changing from 1 to 1.6 hard sphere diameters. For the current state of art in crystallization of confined systems we recommend to consult recent reviews[2,3,22].

In this paper we study the influence of the confinement on the hexatic phase. We investigate a Lennard-Jones fluid at different values of wall-particle attraction during freezing and melting. The system is confined in an attractive slit pore with changing wall separation, being able to accommodate 1 or 2 layers. To characterize and distinguish the liquid, hexatic and solid phases we investigated several order parameters and compared their behavior. We show that the identification of a hexatic phase is depending on the order parameters one uses. There is some controversy in experiments regarding the observation of a hexatic phase[37,38]. We study how strong the system has to be confined to observe a hexatic phase, and whether such a phase can be observed also in multilayer systems, as predicted by Radhakrishnan et al[29,33].

The article is structured as follows. In section II we describe our simulation method, and in section III we present the order parameters and the results. We conclude with a summary IV.

## II. SIMULATION METHOD

We performed molecular dynamics (MD) simulations of Lennard-Jones particles confined between two structureless walls. The particles interact via the LJ-potential

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \tag{1}$$

where $r$ is the distance between the particles, $\sigma$ the particle diameter and $\epsilon$ the depth of the minimum of the LJ potential. The interaction between walls and particles is given by a LJ-potential integrated over semi-space:

$$u_w(r) = 4\epsilon_w \left[ \left( \frac{\sigma}{r} \right)^{9} - \left( \frac{\sigma}{r} \right)^{3} \right]. \tag{2}$$

The particle-particle interaction was cut off and shifted at a distance $r_c = 2.5\sigma$ and the wall-particle interaction at a distance $r_c = 4.0\sigma$, since the wall-particle potential is wider and deeper than the particle-particle potential. For the following we will use $\epsilon$ as the unit of energy, $\sigma$ as the unit of length and $\tau = \sqrt{1 \cdot \sigma^2/\epsilon}$ as unit of time (i. e. use the particle mass as the unit of mass); consequently, temperatures are given in multiples of $\epsilon/k_{\mathrm{B}}T$. The simulations were performed in a cuboid box with periodic boundary conditions in the $x$- and $y$- directions and two walls positioned at $z = 0$ and $z = L_z$. The distance between the walls was chosen such that $n = 1, 2$ layers can be accommodated in the pore, namely $L_z = 2 \cdot 1.12 + 0.916 \cdot (n - 1)$. Here, 1.12 is the distance at which the wall potential has its minimum, and 0.916 is the layer distance in an ideal FCC lattice with spacing one. Therefore $L_z$ was either 2.24 or 3.16 for one or two layers respectively, while the other two dimensions of the simulation box were fixed as $L_x = L_y = 200$. The number of particles $N$ was chosen such that the density was kept constant at one particle per unit cube independent of the width of the slit, and therefore ranged from 44800 for one layer to 81600 particles for two layers. Since the slit is narrow, layering in the two layered system is observed in the whole range of the temperatures.

We carried our simulation out in the NVT ensemble, since this corresponds to the way recent experiments were done[13,26], although our parameters do not strictly allow to reproduce these experiments. The simulations ran $1.0 \times 10^6$ MD steps for equilibration and $2.5 \times 10^5$ MD steps for sampling. For our simulations the software package ESPResSo version 2.1.2j was used[39].

## III. RESULTS AND DISCUSSION

To check whether the system is in a hexatic phase one usually studies the decay of the $G_6$ correlation of the local bond-order parameter, the orientational susceptibility $\chi_6$: the scaling of its mean for different system sizes[27] and its probability distribution for different system sizes[24], to check the homogeneity of the system and for finite size effects. In our work we also study the scaling of a modified susceptibility $\chi_6'$ (fluctuation) for different system sizes and temperatures[13,25,40] and (to our knowledge used only in strictly 2d systems before) the Binder cumulant of $\psi_6$[25,41].

We would like to introduce these parameters at the example of the system accommodating one layer and with the wall attraction $\epsilon_w = 5$. All parameters are based on the local bond-order correlation parameter since the hexatic phase is characterized by quasi long-range bond order. The local bond-order correlation parameter of particle $j$ in layer $m$ at a position $\mathbf{x}_j$ is defined as

$$\psi_6(\mathbf{x}_j) = \frac{1}{N_j} \sum_{k=1}^{N_j} e^{i 6 \theta_{jk}} \tag{3}$$

where $N_j$ is the number of neighbors of particle $j$ within layer m, the sum is over the neighbors $k$ of $j$ within $m$, and $\theta_{jk}$ is the angle between an arbitrary fixed axis and the line connecting particles j and k. The order parameter of the layer $\Psi_6$ is defined as the average over $\psi_6(\mathbf{x}_j)$ for all $N$ particles within the layer

$$\Psi_6 = \frac{1}{N} \left| \sum_{j=1}^{N} \psi_6(\mathbf{x}_j) \right| . \tag{4}$$

The correlation function $G_6(r)$ of the local bond-orientational order helps to distinguish long- and short-range orientational order. It is defined as

$$G_6(r) = \langle \psi_6^*(\mathbf{x}')\psi_6(\mathbf{x}) \rangle \quad , \tag{5}$$

where the average is taken over all particles within a layer where positions $\mathbf{x}'$ and $\mathbf{x}$ are a distance $r$ apart.

The radial distribution function in turn allows to distinguish long- and short-range translational order and it is defined as

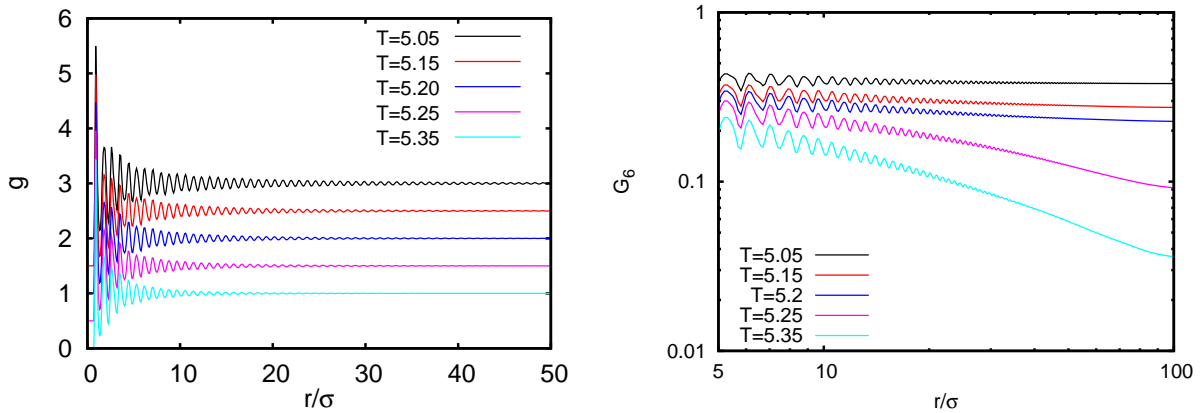$$g(r) = \langle \rho(r) \rangle / \rho \quad , \tag{6}$$

FIG. 1. Left figure: Radial distribution function $g(r)$ for one layer, $\epsilon_w = 5$ versus $r$. The curves are shifted along the y-axis to separate them. The RDF for $T = 5.05, 5.15$ is quasi long-ranged and solid-like, and for $T = 5.2, 5.25$ and $5.35$ it is short-ranged as for liquid.

Right figure: Correlation function $G_6(r)$ of the bond order parameter versus $r$. $G_6$ does not decay for $T = 5.05$, for $T = 5.15$ and $5.2$ it decays algebraically, for $T = 5.25$ and $5.35$ $G_6$ decays exponentially.

where $\langle \rho(r) \rangle$ denotes the average local density at distance $r$ from a fixed particle, and $\rho$ the overall average density.

Ideally, the decay of $G_6$ together with the radial distribution function $g(r)$ (RDF) allow to detect a hexatic phase. For a two-dimensional crystal with long-range orientational and translational order, $G_6$ flattens to a nonzero constant, while $g(r)$ decays very slowly to 1. In a two dimensional liquid we have only short-range order, and therefore both functions decay exponentially to 0 and 1, respectively. In the hexatic phase with its long-range orientational, but short-range translational order, $G_6$ decays algebraically, while $g(r)$ decays exponentially.

As we can see in the Fig.1, the radial distribution for $T = 5.05, 5.15$ is still quasi long-ranged and solid-like, and for $T = 5.2, 5.25$ and $5.35$ the RDF looks like the one for liquid. Meanwhile, $G_6$ only for $T = 5.05$ does not show any decay, for $T = 5.15$ and $5.2$ it decays algebraically and starting with $T = 5.25$ it decays exponentially. Combining conclusions from RDF and $G_6$ one can suspect that around $T = 5.2$ there is a hexatic phase and at $T = 5, 15$ we have a defective crystal. We would also like to note that the crossover to exponential decay at $T = 5.25$ happens at long distances above 20, that means that to make an appropriate judgment about type of decay, one needs sufficiently large boxes.

However, both $G_6$ and the RDF are averaged over the whole system, so if the system is not homogenous, they can not detect that. The obvious way to check the homogeneity, except for a direct observation, is to divide the original system into several subsystems and to compare the behavior of the parameters in each of subbox. Calculating $G_6$ in subsystems is not favorable, since we are interested in the long range decay that becomes impossible to study with decreasing system size.

In reference[24] a study of the nearest-neighbor bond-angular susceptibility on various length scales was performed. The susceptibility is defined as

$$\chi_6 = \left\langle \left| \frac{1}{N} \sum_j \psi_6(\mathbf{x}_j) \right|^2 \right\rangle = \langle \Psi_6^2 \rangle \tag{7}$$

This quantity is used to examine the system on different length scales by dividing the system into equal subblocks of length $L_b = L/2, L/4...L/64, L/128$, where L is the box length of the original system. For each subblock the distribution of $\chi_6$ was computed. In the solid $\chi_6$ will be between 1 and 0.5 due to presence of the long range order and in the liquid $\chi_6$ will be close to zero. In the Fig.2 (left) we show the distribution of $\chi_6$ at $T = 5.2$, where hexatic phase is suspected. One can see that the distribution has one peak, so the phase should be homogeneous at this temperature. The $\chi_6$ peak gradually shifts away from 0.5 and becomes wider with increasing temperature and then, at $T = 5.25$, the system changes into the liquid state (Fig. 2(right)). Again, this supports the idea that at $T = 5.2$ the system goes through a hexatic phase.

If the system is inhomogeneous, a combination of solid and liquid distribution for sub-blocks with small length is observed, a vivid example is shown in Fig.3(right) for the two layers system at $T = 3.8$. In all two layer systems for different wall attraction we could see only three regimes: solid, liquid or a solid-liquid coexistence. As expected, the radial distribution function and the correlation of the bond-order parameter do not capture this (Fig.3(left)). The RDF of up to $T = 3.8$ is still quasi-long-range and then at $T = 3.85$ it becomes short-range. The decay of the $G_6$ at $T = 3.8$ is algebraic, at $T = 3.85$ it shows a combination of algebraic and exponential decays and at $T = 3.9$ it becomes purely exponential (see the insert Fig.3(left)). No homogeneous phase in the intermediate region was observed for any of the wall-particles attractions we studied.

Bagchi et al.[27] analyzed the scaling of the logarithm of the ratio $\chi_6(L_b)/\chi_6(L)$ versus $\ln(L_b/L)$. In the isotropic phase the slope should be $-2$ and in the hexatic phase it will be
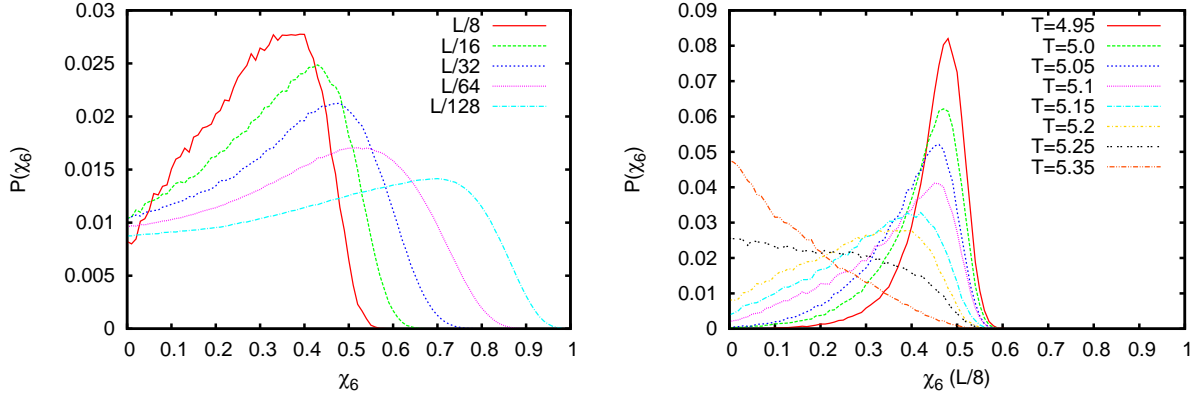
FIG. 2. Left figure: The distribution of $\chi_6$ for different subdivisions of the box at $T = 5.2$ in one layer, $\epsilon_w = 5$, where we suspected a hexatic phase. The distribution has one peak and the phase is homogeneous.

Right figure: The distribution of $\chi_6$ for subdivision $1/8$ at different temperatures. The peak of the distribution gradually shifts away from 0.5 and becomes wider with increasing temperature, then at $T = 5.25$ the system changes into the liquid state

$-\eta_6 \leq -1/4$. For the crystal without defects there should be no scaling. This relation is widely used to check the presence of the hexatic phase and finite size effects. In Fig. 4 we present the results of the scaling for our system. Due to defects in the crystal the scaling for low temperatures is not linear. The dotted line with the slope $-1/4$ reproduces the maximum slope expected in the hexatic phase. As we can see from Fig.4, the slope of the scaling curve for $T = 5.25$ is very close to $1/4$, but we already know that the corresponding $G_6$ decays on long distances exponentially, so, most probably, at this temperature no hexatic phase exits. The scaling for lower temperatures does not allow us to distinguish between a crystal with many defects and a probable hexatic phase. The scaling for $T = 5.2$, where we expected the hexatic behavior, does not look any different from the one for $T = 5.15$, that we verified as a crystal.

Another version of susceptibility[25,40], $\chi_6'(L_B)$, measures the fluctuations of the bond-order parameter in the system:

$$k_B T \chi_6' = L^2 \left( \langle \Psi_6^2(L_b) \rangle - \langle \Psi_6(L_b) \rangle^2 \right), \tag{8}$$

It should show a dramatic increase as the transition temperatures are approached either from solid or from liquid phases and for the hexatic region it should become infinite[25]. However,
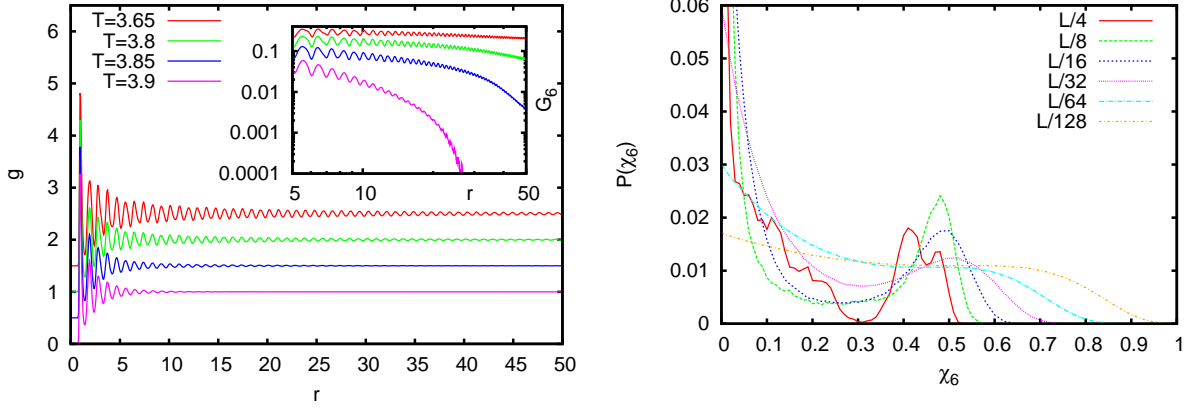
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FIG. 3. Left figure: In 2 layers the radial distribution function for $T = 3.65$ and $T = 3.8$ still behaves solid-like and for $T = 3.85$ and $T = 3.9$ it shows the liquid-like behavior.

Inset: Correlation of the bond order parameter $G_6$ decays algebraically up to $T = 3.8$, for $T = 3.85$ it has at first an algebraic decay and that becomes later exponential, at $3.9$ $G_6$ decays exponentially.

Right figure: The distribution of $\chi_6$ for different subdivisions of the box at $T = 3.8$ in two layers, $\epsilon_w = 5$. The distribution has two peaks around $0.5$ and $0$, that shows that the system has a liquid-solid coexistence.

it is impossible to produce infinity in the simulations. In Fig. 5 (left) the behavior of $\chi_6'$ as a function of temperature is presented. We present our results both for our standard system with $L_y = L_z = 200$ and a smaller one $L_y = L_z = 100$ to show that the size effects are very small. We compare $\chi_6'$ for subdivisions $L/64$ and $L/128$ in the bigger system that correspond to $L/32$ and $L/64$ in the smaller system. We can see that the maxima of all curves are shifted to the liquid phase to $T = 5.35$, which is a consequence of the finite size effects in first order transitions[25,42]. The dashed line marks the temperature $T = 5.2$, where some signs of the hexatic phase were observed, here we do not see any special features. The right part of Fig. 5 displays the dependence of $\chi_6'$ on the inverse value of the length of a subbox. If we do not subdivide the box, the scaling breaks down as we can clearly see on the graphs (first points). This failure can be explained by the fact that we simulate in the canonical ensemble, but as soon as we start subdividing the system, it behaves more like a grand-canonical ensemble. Unfortunately, we cannot extrapolate our curves to $\chi_\infty$ as it was done in[25] since our way of subdivision does not provide enough data in the linear region of the curve. What we can still see is that the steepest slope is observed for temperatures $5.35$
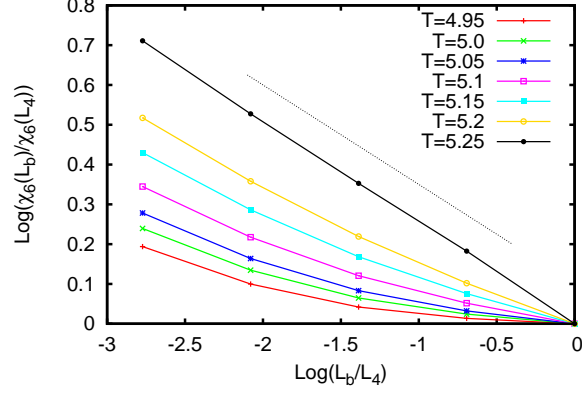
FIG. 4. Subblock scaling analysis for $\chi_6$, in one layer, $\epsilon_w = 5$. Dotted line corresponds to the slope $-1/4$, the maximum possible slope for a hexatic phase. The slope of $\chi_6$ at $T = 5.25$ is close to $-1/4$, for other temperatures it is lower. The observed nonlinearity is due to defects.
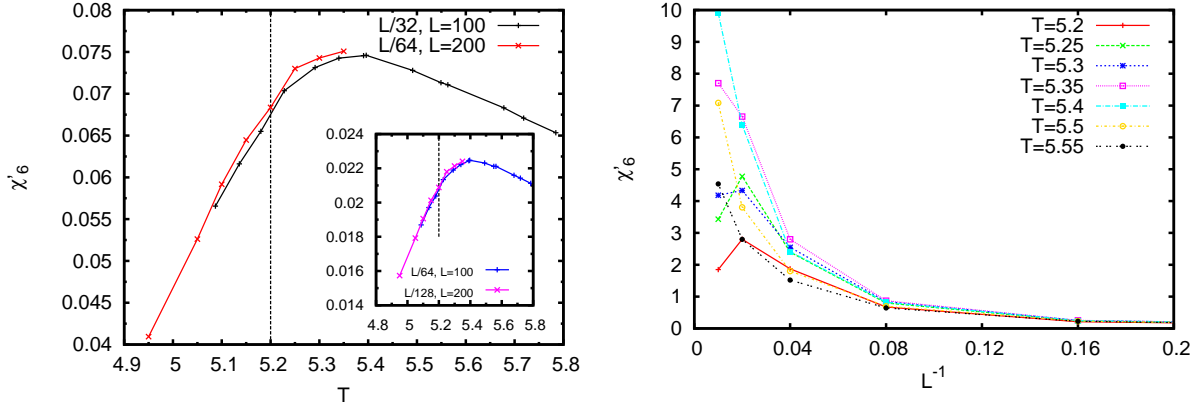


FIG. 5. Left figure: Fluctuation of the bond-order parameter, $\chi_6'$, as a function of temperature, in one layer, $\epsilon_w = 5$ for systems with box-lengths 100 and 200 for different subdivisions. The dashed line marks $T = 5.2$, where we suspected a hexatic phase. The maxima of the curves are shifted to the liquid region. Size effects are small.

Right figure: $\chi_6'$ as a function of the inverse value of the length of a subbox. The steepest slopes are observed for temperatures 5.35 and 5.40, both in the liquid phase.

and 5.40, and we already know both that temperatures lie in the liquid state region. We can conclude that the observed transition is of a first order, but, as expected, the transition temperatures obtained with this parameter are too high.

The last order parameter we investigate is the Binder cumulant[25,41]:

$$U_L = 1 - \frac{\langle \Psi^4 \rangle_6}{3\langle \Psi^2 \rangle_6^2}. \tag{9}$$

Away from criticality in the limit of infinite system size, the cumulant assumes different limiting values for ordered and disordered phases. For finite systems the value of the cumulant depends on the system size: the smaller the system the more the cumulant deviates from the limiting value. In the case of a first order transition the cumulant exhibits an effective common intersection point at the transition for sufficiently large systems. As for the hexatic phase the cumulant is expected to be independent of the system size and to collapse onto one line over the entire range of the phase. Fig. 6 (left) presents the behavior of the cumulant with temperature (lines serve as guides to the eye). We see clearly that there is only one intersection point, meaning that there is one first order solid-liquid transition and no hexatic phase.

Summarizing all our investigations we have shown that one should be quite careful in choosing the order parameters in order to claim to have observed a hexatic phase. In our case, the Binder cumulant provided the most stringent test. The correlation function of the bond-order parameter should be studied on big scales, since the crossover from the algebraic decay to exponential can happen at relatively large distances. If scaling of the susceptibility does not give a straight line, that most probably means that we observe a very defective crystal, but not a hexatic phase.

What would happen if the attraction of the walls becomes even more attractive? Let us look at the case $\epsilon_w = 7$. We will start from the last parameter we considered previously, $U_l$ given by Eqn.(9), since we claimed that this was the most sensitive parameter. As one can see in Fig.6 (right), there is a small interval for temperatures between 5.44 and 5.46 where the curves for different sub-divisions of the system almost fall together. We interprete this as a sign of a possible hexatic phase, since here the cumulant is independent of the system size. However, the temperature interval is extremely narrow, so that the collapse of $U_l$ might not show a new phase itself, but might be a precursor of a hexatic phase that would appear at higher wall attraction or might happen only for infinite wall attraction.

The distribution of $\chi_6$ (7) in the possible hexatic phase, $T = 5.45$, shows that the system is homogeneous (Fig. 7 left). If we look at the behavior of the $\chi_6$ distribution (Fig. 7 right), taking as an example the subdivison into $8 \times 8$ subblocks, we observe again that the
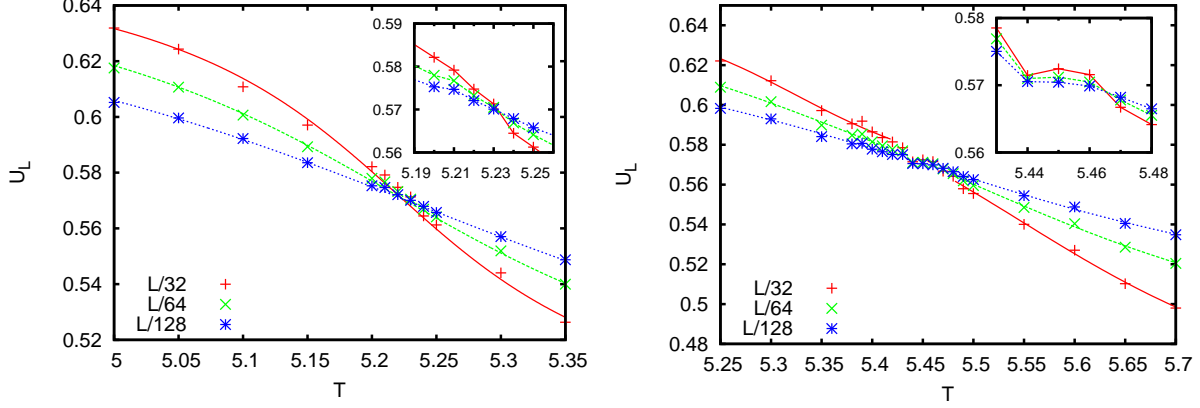
FIG. 6. Left figure: The Binder cumulant $U_l$ for several subdivisions of the system in one layer, $\epsilon_w = 5$ as a function of temperature. The curves do not collapse anywhere and intersect around $T = 5.23$ (see inset), meaning that there is one first order solid-liquid transition and no hexatic phase. Lines are guides to the eye.

Right figure: The Binder cumulant $U_l$ for several subdivisions of the system in one layer, $\epsilon_w = 7$. The curves are almost collapsing on one curve between temperatures 5.44 and 5.46 (see inset), a sign of a possible hexatic phase. Lines are guides to the eye.

peak of the distribution decreases and slowly moves to lower values of $\chi_6$ with increasing temperature. We do not see any peculiarities in the distribution for $T = 5.45$, and at $T = 5.55$ we observe a change to the characteristic liquid distribution with the maximum at 0.

Also the behavior of other parameters, like the radial distribution function and the correlation of the bond-order parameter or scaling of $\chi_6$, does not qualitatively differ from the behavior in the case of a less attractive wall $\epsilon_w = 5$, so we go through them briefly.

The correlation of the bond-order parameter decays algebraically for temperatures up to $T = 5.5$ (inset of Fig. 8), and at $T = 5.35$ and further on we see a short-range behavior of the radial distribution function (Fig. 8). However, we already know that for $T = 5.35$ and 5.4 there is no hexatic phase and we deal with a defective crystal. So, we conclude, that a combination of RDF and $G_6$ is unreliable for claiming the occurence of a hexatic phase, since it does not distinguish it from a defective crystal.

The scaling of the $\chi_6(L_b)/\chi_6(L_0)$ for temperatures up to $T = 5.45$ is below the 1/4 slope (Fig. 9). For $T = 5.5$ the scaling of the ratio is exactly 0.25. The distribution of $\chi_6$ for 5.5 is
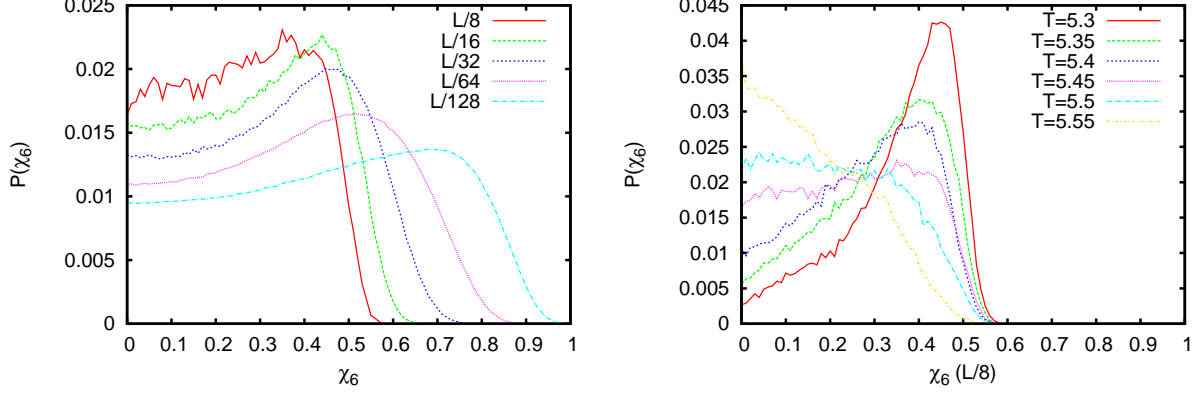
FIG. 7. Left figure: The distribution of $\chi_6$ for different subdivisions of the box in hexatic phase at $T = 5.45$ in one layer, $\epsilon_w = 7$. The distribution has one peak and the phase is homogeneous.

Right figure: The distribution of $\chi_6$ for subdivision $1/8$ at different temperatures. The peak of the distribution gradually shifts away from 0.5 and becomes wider with increasing temperature and then at $T = 5.55$ the system changes into the liquid state
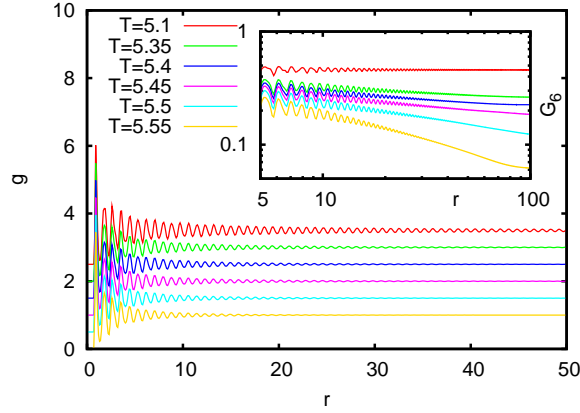


FIG. 8. Radial distribution function $g(r)$ for one layer, $\epsilon_w = 7$. The curves are shifted along the y-axis to separate them. RDF for $T = 5.1$ is quasi long-ranged and solid-like, already at $T = 5.35$ it is short-ranged as for liquid.

Inset: Correlation of the bond-order parameter $g_6$ in one layer, $\epsilon_w = 7$. For $T = 5.1$ it does not decay, for $T = 5.35, 5.4, 5.45, 5.5$ it decays algebraically and for $T = 5.55$ $G_6$ decays exponentially.

also not yet liquid (Fig. 7). Therefore, according to distribution and scaling of $\chi_6$ and $G_6$ at the temperature 5.5 the system has hexatic properties, but for the cumulant $U_l$ it is already in the liquid phase. On the one hand, since we do not observe any two-phase region between
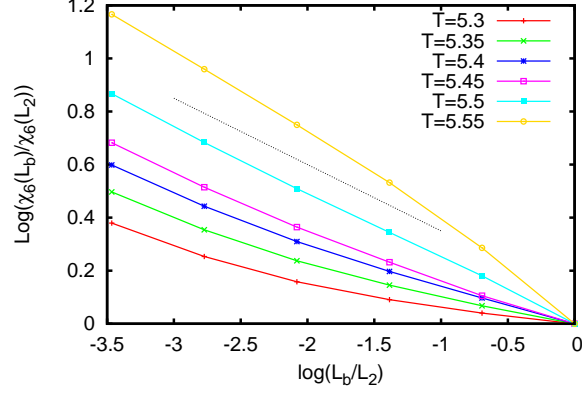
14

FIG. 9. Subblock scaling analysis for $\chi_6$, in one layer, $\epsilon_w = 7$. Dotted line corresponds to the slope $-1/4$, the maximum possible slope for a hexatic phase.

a hexatic and liquid phase, one can assume that the Binder cumulant is oversensitive and can omit some points. On the other hand, the transition from the hexatic to the liquid state proceeds very smoothly and the temperature 5.5 can be treated as a boundary temperature between two phases.

If we look at the change of $\chi_6'(L)$ (8) with temperature, we observe maxima between the temperatures 5.6 and 5.65 (Fig. 10), which indicate that the transition to the liquid is of first order, since the maxima for this parameter are far in the liquid phase. However, no change in behavior is observed in the possible region of a hexatic phase, the borders of which are marked with dashed lines. We compare again the behavior of $\chi_6'(L)$ for subdivisions $L/64, L/128$ in our standard system with box-length 200 and $L/32, L/64$ in a smaller one with $L_y = L_z = 100$. The curves for the corresponding subdivisions coincide in the solid without defects and the liquid region. They show a small quantitative difference when the crystal gains defects and then goes to the hexatic phase, which region is marked by two dashed lines.

We have shown that only the Binder cumulant behaves qualitatively different for the systems with $\epsilon_w = 5$ and $\epsilon_w = 7$. The behavior of the other parameters is similar for both cases. In our simulations, the Binder cumulant shows signs of a hexatic phase only at the strongest wall attraction $\epsilon_w = 7$. We checked the fluctuations of particles perpendicular to the walls by fitting the density profile to a Gaussian distribution. The fluctuation for $\epsilon_w = 5$ is $\Delta z \approx 0.175$ and $\Delta z \approx 0.15$ for $\epsilon_w = 7$, practically independent of the temperature in
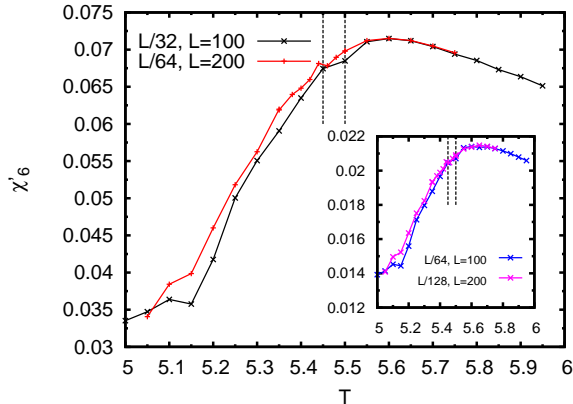
15

FIG. 10. Fluctuation of the bond-order parameter, $\chi'_6$, as a function of temperature, in one layer, $\epsilon_w = 7$, for systems with box-lengths 100 and 200 for $L/32$ and $L/64$ subdivisions correspondingly. Dashed lines mark the region of a hexatic phase. Maximums of curves are shifted to the liquid region. The size effects are small. Inset shows $\chi'_6$ for $L/64$ and $L/128$.

the studied range. Both values are significantly smaller than 0.4, which was reported to be the maximally possible fluctuations for liquid-to-hexatic transition in the quasi-2D system of hard spheres[36]. Since our Lennard-Jones particles are much softer than hard spheres and therefore can overlap to some extent, this might explain why we need a stricter confinement to observe a hexatic phase.

## IV. CONCLUSIONS

We carried out a simulation study of the liquid-to-solid transformation of a LJ fluid in a slit pore accommodating one or two layers and several ratios of wall-particle to particle-particle attractions. To investigate the possible existence of an intermediate hexatic phase that was previously observed not only in 2d, but also in quasi-2d systems[10,29,36], we performed an analysis using a broad range of order parameters. Studying the radial distribution function together with the decay of the bond-order correlation turned out to be insufficient, since, on the one hand, they characterize the system in a whole, so one can not conclude from their behavior if the system is homogeneous. On the other hand, they are also insensitive to defects, so one cannot distinguish properly between a defective crystal and a hexatic phase. The scaling of different parameters turned out to be much more successful. With the help of

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the angular susceptibility one can easily check the homogeneity of the system. We consider the Binder cumulant to be the most reliable parameter in distinguishing a hexatic phase, since it shows either existence or absence of it. In our study the temperature of transition computed with the help of $U_L$ does not coincide with the temperature where the fluctuation of the bond-order parameter has a maximum, which makes it possible to assume a first order transition in all cases[25]. We observed signs of a possible intermediate hexatic phase only in the slit with extremely attractive walls and a single layer of particles, i. e. if the system is practically 2d, otherwise there is a single liquid-solid transition. This is in contrast to the works[29,33] on a similar system, in which signs of a hexatic phase in the contact layers near the wall were observed even in systems with up to seven layers, at wall strengths comparable to our $\epsilon_w = 7$. These findings, however, were based on studying the behavior of global order parameters and scaling of $\Psi_6$ only, which, as we have shown, are not sufficient to safely detect a hexatic phase.

Our results have implications for experimental studies on the hexatic phase[11,14], since they show that even a monolayer requires a strong confining force to exhibit a true hexatic phase, while studies based on the decay of the RDF and $G_6$ can easily be fooled by defective crystals or coexistent phases. This might explain why some studies find a hexatic phase, while other studies of a seemingly very similar system do not.

**REFERENCES**

[1]C. Alba-Simionesco, B. Coasne, G. Dosseh, G. Dudziak, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, J. Phys.: Cond. Matt. **18**, R15 (2006).

[2]U. Gasser, J. Phys.: Cond. Matt. **21**, 203101 (2009).

[3]U. Gasser, C. Eisenmann, G. Maret, and P. Keim, ChemPhysChem **11**, 963 (2010).

[4]L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Progr. Phys. **62**, 1573 (1999).

[5]M. Miyahara and K. E. Gubbins, J. Chem. Phys. **106**, 2865 (1997).

[6]V. N. Ryzhov and E. E. Tareyeva, Phys. Rev. B **51**, 8789 (1995).

[7]V. Ryzhov and E. Tareyeva, Physica A **314**, 396 (2002).

[8]C. H. Mak, Phys. Rev. E **73**, 065104 (2006).

[9]S. I. Lee and S. J. Lee, Phys. Rev. E **78**, 041504 (2008).

[10]K. Binder, S. Sengupta, and P. Nielaba, J. Phys.: Cond. Matt. **14**, 2323 (2002).

[11]C. A. Murray and D. H. Van Winkle, Phys. Rev. Lett. **58**, 1200 (1987).

[12]A. H. Marcus and S. A. Rice, Phys. Rev. Lett. **77**, 2577 (1996).

[13]Y. Han, N. Y. Ha, A. M. Alsayed, and A. G. Yodh, Phys. Rev. E **77**, 041406 (2008).

[14]K. Zahn, R. Lenke, and G. Maret, Phys. Rev. Lett. **82**, 2721 (1999).

[15]K. Zahn and G. Maret, Phys. Rev. Lett. **85**, 3656 (2000).

[16]P. Keim, G. Maret, and H. H. von Grünberg, Phys. Rev. E **75**, 031402 (2007).

[17]J. M. Kosterlitz and D. J. Thouless, J. Phys. C: Solid State Phys. **6**, 1181 (1973).

[18]B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).

[19]D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[20]A. P. Young, Phys. Rev. B **19**, 1855 (1979).

[21]K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).

[22]S. Rice, Chemical Physics Letters **479**, 1 (2009).

[23]K. Wierschem and E. Manousakis, Physics Procedia **3**, 1515 (2010), Proceedings of the 22th Workshop on Computer Simulation Studies in Condensed Matter Physics (CSP 2009).

[24]K. J. Strandburg, J. A. Zollweg, and G. V. Chester, Phys. Rev. B **30**, 2755 (1984).

[25]H. Weber, D. Marx, and K. Binder, Phys. Rev. B **51**, 14636 (1995).

[26]Y. Peng, Z. Wang, A. M. Alsayed, A. G. Yodh, and Y. Han, Phys. Rev. Lett. **104**, 205703 (2010).

[27]K. Bagchi, H. C. Andersen, and W. Swope, Phys. Rev. Lett. **76**, 255 (1996).

[28]A. Jaster, Physics Letters A **330**, 120 (2004).

[29]R. Radhakrishnan, K. E. Gubbins, and M. Sliwinska-Bartkowiak, Phys. Rev. Lett. **89**, 076101 (2002).

[30]H. Bock, K. Gubbins, and K. Ayappa, J. Chem. Phys. **122**, 094709 (2005).

[31] K. Ayappa and R. Mishra, J. Phys. Chem. B **111**, 14299 (2007).

[32] M. Kahn, J.-J. Weis, C. Likos, and G. Kahl, Soft Matter **5**, 2852 (2009).

[33] R. Radhakrishnan, K. E. Gubbins, and M. Sliwinska-Bartkowiak, J. Chem. Phys. **116**, 1147 (2002).

[34] A. Vishnyakov and A. V. Neimark, J. Chem. Phys. **118**, 7585 (2003).

[35] A. J. Page and R. P. Sear, Phys. Rev. E **80**, 031605 (2009).

[36] X. Xu and S. A. Rice, Phys. Rev. E **78**, 011602 (2008).

[37] A. H. Marcus and S. A. Rice, Phys. Rev. E **55**, 637 (1997).

[38] P. Karnchanaphanurach, B. Lin, and S. A. Rice, Phys. Rev. E **61**, 4036 (2000).

[39] H. J. Limbach, A. Arnold, B. A. Mann, and C. Holm, Comp. Phys. Comm. **174**, 704 (2006).

[40] J. Lee and K. J. Strandburg, Phys. Rev. B **46**, 11190 (1992).

[41] K. Binder, Z. Phys. B **43**, 119 (1981).

[42] W. Strepp, S. Sengupta, and P. Nielaba, Phys. Rev. E **63**, 046106 (2001).